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(54) **Golf ball**

(57) A golf ball includes, as a composing element, a hot-molded product obtained from a rubber composition which includes a main rubber containing 10 to 90 mass% of a polybutadiene, an unsaturated carboxylic acid and/or a metal salt thereof, and an organic peroxide. The polybutadiene has 60% or more of cis-

1,4-bonds. Further, letting a Mooney viscosity (ML_{1+4} (100°C)) of the polybutadiene be ML and a viscosity of a toluene solution containing 5 mass% of the polybutadiene at 25°C be η (mPa·s), ML and η satisfy a relationship of $\eta \geq 20 \times ML - 600$.

DescriptionBACKGROUND

5 [0001] The present invention relates to a golf ball including a molded body obtained using a particular kind of polybutadiene, with a view to achieving high resilience.

Prior Art

10 [0002] Conventionally, to give excellent resilience to a golf ball, various attempts have been made to improve the composition of a polybutadiene used as a main rubber for the golf ball.

[0003] For example, Japanese Patent Laid-open No. Sho 62-89750 has proposed a rubber composition for a solid golf ball, which contains, as a main rubber, a polybutadiene having a Mooney viscosity ranging from 70 to 100 and synthesized by using an Ni or Co catalyst and a polybutadiene having a Mooney viscosity ranging from 30 to 90 and synthesized by using a lanthanum based catalyst or a polybutadiene having a Mooney viscosity ranging from 20 to 50 and synthesized by using an Ni or Co catalyst.

[0004] The above-described golf ball, however, has been further required to be improved in terms of resilience of the ball.

20 [0005] Japanese Patent Laid-open No. Hei 2-268778 has proposed a golf ball, which is produced from a rubber composition containing a polybutadiene having a Mooney viscosity of less than 50 and synthesized by using a group VIII element catalyst and a polybutadiene having a Mooney viscosity of less than 50 and synthesized by using a lanthanide catalyst. The golf ball thus obtained, however, is poor in resilience.

[0006] Japanese Patent Laid-open No. Hei 11-70187 has proposed a multi-piece solid golf ball including an intermediate layer made from a polybutadiene having a low Mooney viscosity; Japanese Patent Laid-open No. Hei 11-319148 has proposed a solid golf ball produced from a rubber composition containing a polybutadiene having a Mooney viscosity ranging from 50 to 60 and synthesized by using an Ni or Co catalyst and a polybutadiene having a Mooney viscosity ranging from 20 to 90 and synthesized by using lanthanoid based catalyst; Japanese Patent Laid-open No. Hei 11-164912 has proposed a solid golf ball produced from a rubber composition in which the amount of 1,2-vinyl bonds is in a range of 2.0% or less and a ratio (Mw/Mn) of a weight-average molecular weight to a number-average molecular weight is in a range of 3.5 or less; Japanese Patent Laid-open No. Sho 63-275356 has proposed a golf ball produced from a rubber composition containing a polybutadiene having a high Mooney viscosity; and Japanese Patent Laid-open No. Hei 3-151985 has proposed a golf ball produced from a rubber composition containing a polybutadiene having a high number-average molecular weight and a polybutadiene having a low number-average molecular weight. There is nevertheless a prevailing desire to find new and useful rubbers for golf balls and in particular to provide good or improved resilience, which is to some extent wanting in the prior art.

35 [0007] In view of the foregoing, the present inventor has earnestly examined and found that a golf ball including, as a composing element, a hot-molded product obtained from a rubber composition which includes a main rubber containing 10 to 90 mass% of a polybutadiene (a), an unsaturated carboxylic acid and/or a metal salt thereof, and an organic peroxide, wherein the polybutadiene has 60% or more of cis-1,4-bonds, and letting a Mooney viscosity ($ML_{1+4}(100^{\circ}C)$) of the polybutadiene be ML and a viscosity of a toluene solution containing 5 mass% of the polybutadiene at $25^{\circ}C$ be η (mPa · s), ML and η satisfy a relationship of $\eta \geq 20 \times ML - 600$, is advantageous in that a very excellent hot-molded product can be obtained by a synergism effect of the polybutadiene having a very high linearity of rubber molecules and the other components, and that a golf ball having such a hot-molded product has very excellent resilience, thereby increasing the carry of the ball. On the basis of the above knowledge, the present invention has been accomplished.

45 [0008] Accordingly, the present invention provides the following golf balls:

(1) A golf ball including, as a composing element, a hot-molded product obtained from a rubber composition, the rubber composition including:

50 a main rubber containing 10 to 90 mass% of a polybutadiene (a);
an unsaturated carboxylic acid and/or a metal salt thereof; and
an organic peroxide;

55 wherein the polybutadiene has 60% or more of cis-1,4-bonds; and
letting a Mooney viscosity ($ML_{1+4}(100^{\circ}C)$) of the polybutadiene be ML and a viscosity of a toluene solution containing 5 mass% of the polybutadiene at $25^{\circ}C$ be η (mPa · s), ML and η satisfy a relationship of $\eta \geq 20 \times ML - 600$.
(2) A golf ball according to (1) above wherein the polybutadiene component (a) is synthesized by using a rare

earth element based catalyst.

(3) A golf ball according to (1) or (2) above wherein the polybutadiene component (a) is synthesized by using a rare earth element based catalyst, and is then reacted with a terminal denaturant.

(4) A golf ball according to any one of (1) to (3) above

wherein the main rubber contains, in addition to the polybutadiene component (a), 90 to 10 mass% of a polybutadiene (b) having a Mooney viscosity of 55 or less.

[0009] Methods of making the disclosed golf balls comprising moulding the mentioned rubber compositions, optionally including blending the rubber compositions from the main (base) rubber, are another aspect of the invention.

DETAILED DESCRIPTION

[0010] Hereinafter, the present invention will be described in detail. A golf ball of the present invention includes a hot-molded product obtained from a rubber composition. The rubber composition includes a main rubber containing 10 to 90 mass% of a polybutadiene (a), wherein the polybutadiene has 60% or more of cis-1,4-bonds, and letting a Mooney viscosity ($ML_{1+4}(100^\circ C)$) of the polybutadiene be ML and a viscosity of a toluene solution containing 5 mass% of the polybutadiene at $25^\circ C$ be η (mPa · s), ML and η satisfy a relationship of $\eta \geq 20 \times ML - 600$.

[0011] The polybutadiene component (a) is required to have the cis-1,4-bonds in an amount of 60% or more, preferably, 80% or more, more preferably, 90% or more, most preferably, 95% or more. If the amount of the cis-1,4-bonds is excessively small, the resilience is reduced.

[0012] The polybutadiene component (a) of the present invention is required to be specified such that letting a Mooney viscosity ($ML_{1+4}(100^\circ C)$) of the polybutadiene be ML and a viscosity of a toluene solution containing 5 mass% of the polybutadiene at $25^\circ C$ be η (mPa · s), ML and η satisfy a relationship of $\eta \geq 20 \times ML - 600$, preferably, $\eta \geq 20 \times ML - 580$, more preferably, $\eta \geq 20 \times ML - 560$, most preferably, $\eta \geq 20 \times ML - 540$. Since the polybutadiene with the viscosities η and ML optimized has a high linearity of polybutadiene molecules, it can give very excellent resilience to a molded-product.

[0013] The polybutadiene component (a) of the present invention may be further specified such that the upper limit of the viscosity η be in a range of $\eta \leq 20 \times ML - 100$, preferably, $\eta \leq 20 \times ML - 150$, more preferably, $\eta \leq 20 \times ML - 200$, most preferably, $\eta \leq 20 \times ML - 250$.

[0014] The viscosity η (mPa · s) of a toluene solution containing 5 mass% of a polybutadiene at $25^\circ C$ used herein is determined by a manner of dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene, and measuring a viscosity of the toluene solution under a condition with $25^\circ C$ using a viscometer constituting standard solution (JIS Z8809) by a specific viscometer.

[0015] The Mooney viscosity used herein is an industrial index of viscosity measured by a Mooney viscometer which is one kind of a rotary plastimeter under JIS-K6300. The Mooney viscosity is expressed in $ML_{1+4}(100^\circ C)$, where M indicates the Mooney viscosity, L indicates a large rotor (L-type) of the plastimeter, "(1+4)" indicates that a preheating time is one minutes and a rotational time of the rotor is four minutes, and " $100^\circ C$ " indicates a measurement temperature.

[0016] The Mooney viscosity [$ML_{1+4}(100^\circ C)$] of the polybutadiene component (a) is required to be in a range of 20 or more, preferably, 30 or more, more preferably, 40 or more, most preferably, 50 or more, with the upper limit being in a range of 80 or less, preferably, 70 or less, more preferably, 65 or less, most preferably, 60 or less.

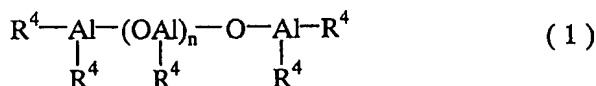
[0017] The polybutadiene component (a) of the present invention is required to be synthesized by using a catalyst, preferably a rare earth element based catalyst.

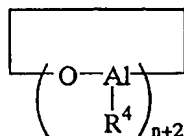
[0018] As the catalyst, there can be used a known type such as lantern series rare earth element compound, an organic aluminum compound, alumoxane, a halogen containing compound, or a combination thereof with a Lewis base.

[0019] Examples of the lanthan series rare earth element compounds may include a halide, a carboxylate, an alcoholate, a thioalcoholate, and an amide of a metal having an atomic number of 57 to 71.

[0020] As the organic aluminum compound, there can be used a compound expressed, for example, by $AlR^1R^2R^3$ (R^1 , R^2 and R^3 may be identical to each other or different from each other, and each of R^1 , R^2 and R^3 is a residual hydrocarbon group having the hydrogen or carbon number of 1 to 8).

[0021] As the alumoxane, there is preferably used a compound having a structure expressed by the following chemical formula (1) or (2):





(2)

[0022] In each chemical formula, R^4 is a hydrocarbon group containing carbon atoms of the carbon number of 1 to 20, and n is an integer of 2 or more.

[0023] In addition, an associated body of the alumoxane as described in "Fine Chemical, 23, (9), 5 (1994)", "J. Am. Chem. Soc., 115, 4971 (1993)", or "J. Am. Chem. Soc., 117, 6465 (1995)" may be used.

[0024] As the halogen containing compound, there can be used an aluminum halide expressed by $\text{AlX}_n\text{R}_{3-n}$ (X is a halogen, R is a residual hydrocarbon group having the carbon number of 1 to 20, for example, an alkyl group, aryl base, or aralkyl base, and n is 1, 1.5, 2 or 3), a strontium halide such as Me_3SrCl , Me_2SrCl_2 , MeSrHCl_2 , MeSrCl_3 , or a metal halide such as silicon tetrachloride, tin tetrachloride, or titanium tetrachloride.

[0025] The Lewis base can be used for complexing the lanthan series rare earth element compound. For example, acetyl acetone or ketone alcohol can be used as the Lewis base.

[0026] In particular, we note that the use of a neodymium base catalyst using a neodymium compound as the lanthan series rare earth element compound advantageously allows production of a polybutadiene containing a large amount of the cis-1,4-bonds and a small amount of the 1,2-vinyl bonds with an excellent polymerization activity. The concrete example of such rare earth element based catalyst has been described in Japanese Patent Laid-open No. Hei 11-35633.

[0027] For the catalytic polymerization of butadiene monomers e.g. by rare earth element catalyst, a solvent may be used, or any solvent may be not used. In the latter case, butadiene monomers may be subjected to bulk polymerization or a vapor-phase polymerization. The polymerization temperature may be in a range of 30 to 150°C, preferably, 10 to 100°C.

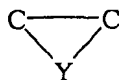
[0028] The polybutadiene component (b) of the present invention may be obtained by polymerization using a catalyst as specified above, followed by reaction of active terminals of the polymer with a terminal denaturant.

[0029] As the terminal denaturants, there can be used e.g. the following known compounds (1) to (6):

(1) A halogenated organic metal compound, a halogenated metal compound, or an organic metal compound expressed by $\text{R}^5_n\text{M}'\text{X}_{4-n}$, $\text{M}'\text{X}_4$, $\text{M}'\text{X}_3$, $\text{R}^5_n\text{M}'(-\text{R}^6-\text{COOR}^7)_{4-n}$, or $\text{R}^5_n\text{M}'(-\text{R}^6-\text{COR}^7)_{4-n}$ (in the chemical formula, R^5 and R^6 may be identical to each other or different from each other, and each of R^5 and R^6 is a hydrocarbon group containing carbon atoms of the carbon number of 1 to 20; R^7 is a hydrocarbon group containing carbon atoms of the carbon number of 1 to 20, which may contain a carbonyl group or ester group at a side chain; M' is a tin atom, silicon atom, germanium atom, or phosphorus atom; X is a halogen atom; and n is 0 or an integer selected from 1 to 3).

(2) A heterocumulene compound containing, in molecules, $\text{Y}=\text{C}=\text{Z}$ bonds (in the formula, Y is a carbon atom, oxygen atom, nitrogen atom, or sulfur atom; Z is an oxygen atom, nitrogen atom, or sulfur atom).

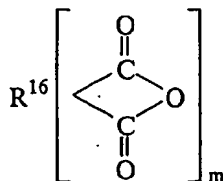
(3) A hetero-tricyclic compound containing, in molecules, bonds expressed by the following chemical formula:



In the chemical formula, Y is an oxygen atom, nitrogen atom, or sulfur atom.

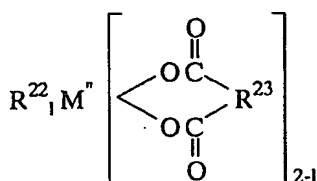
(4) A halogenated isocyano compound.

(5) $\text{R}^8\text{-CCOOH}$, $\text{R}^9(\text{COX})_m$, $\text{R}^{10}\text{-(COO-R}^{11})$, $\text{R}^{12}\text{-OCOO-R}^{13}$, $\text{R}^{14}\text{-(COOCO-R}^{15})_m$, or a carboxylic acid, an acid halide, an ester compound, a carbonic ester compound, or an acid anhydride, which is expressed by the following chemical formula:



In the formula, R^8 to R^{16} may be identical to each other or different from each other, and each of R^8 to R^{16} is a hydrocarbon group containing carbon atoms of the carbon number of 1 to 50, X is a halogen atom, and m is an integer selected from 1 to 5.

(6) R^{17}_1 , $M''(\text{OCOR}^{18})_{4-1}$, $R^{19}_1 M''(\text{OCO-R}^{20}\text{-COOR}^{21})_{4-1}$, or a metal salt of a carboxylic acid expressed by the following chemical formula:



[0030] In the chemical formula, R^{17} to R^{23} may be identical to each other or different from each other, and each of R^{17} to R^{23} is a hydrocarbon group containing carbon atoms of the carbon number of 1 to 20, M'' is a tin atom, silicon atom, or germanium atom, 1 is 0 or an integer selected from 1 to 3.

[0031] Examples of terminal denaturants shown in each of the above items (1) to (6) and a method of allowing the terminal denaturant to react with active terminals of a polymer have been disclosed, for example, in Japanese Patent Laid-open Nos. Hei 11-35633 and Hei 7-268132.

[0032] The main rubber is required to contain the polybutadiene component (a) in an amount of 10 mass% or more, preferably, 20 mass% or more, more preferably, 30 mass% or more, most preferably, 40 mass% or more, with the upper limit being in a range of 90 mass% or less, preferably, 80 mass% or less, more preferably, 70 mass% or less, most preferably, 60 mass% or less. If the content of the polybutadiene component (a) is out of the above range, the resilience of the molded product is reduced, thereby failing achieve the function and effect of the present invention. The nature of a further rubber component (b) of the main rubber of the present invention is not such a critical factor in the rubber composition of the present invention. It may be added in such a range as not to obstruct the object of the present invention, as needed. Examples of suitable other rubbers for component (b) may include polybutadiene rubber (BR), styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDR). These materials may be added singly or in combination of two kinds or more. Preferably, to improve the resilience, and the moldability such as workability in extrusion of the rubber composition, the other rubber component (b) may be a polybutadiene other than the polybutadiene component (a), wherein the Mooney viscosity of the polybutadiene may be in a range of 55 or less, preferably, 50 or less, more preferably, 47 or less, most preferably, 45 or less, with the lower limit being in a range of 10 or more, preferably, 20 or more, more preferably, 25 or more, most preferably, 30 or more.

[0033] Such polybutadiene component (b) is recommended to be synthesized by using a group VIII element catalyst, for example, a nickel based catalyst or a cobalt based catalyst.

[0034] Examples of the nickel based catalysts may include a one-component type such as nickel diatomaceous earth; a two-component type such as Raney-nickel/titanium tetrachloride; and a three-component type such as a nickel compound/organic metal/boron trifluoride etherate. Examples of nickel compounds may include reduced nickel with carrier, Raney-nickel, nickel oxide, nickel carboxylate, and a complex salt of organic nickel. Examples of the organic metals may include a trialkyl aluminum such as triethyl aluminum, tri-n-propyl aluminum, tri-isobutyl aluminum, or tri-n-hexyl aluminum; an alkyl lithium such as n-butyl lithium, sec-butyl lithium, tert-butyl lithium, or 1,4-dibutane lithium; and a dialkyl zinc such as diethyl zinc or dibutyl zinc.

[0035] Examples of the cobalt based catalysts may include, as cobalt and compounds thereof, Raney-cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyl dithiocarbamate, cobalt anilinium nitrite, and cobalt dinitrosyl chloride. In particular, each of these compounds is preferably combined with a dialkyl aluminum monochloride such as diethyl aluminum monochloride or diisobutyl aluminum monochloride, a trialkyl aluminum such as triethyl aluminum,

tri-n-propyl aluminum, triisobutyl aluminum or tri-n-hexyl aluminum, an aluminum alkyl sesquichloride such as ethyl aluminum sesquichloride, or aluminum chloride.

[0036] The polymerization of butadiene monomers by using the above group VIII element based catalyst, particularly, a nickel or cobalt based catalyst can be generally performed by continuously charging the butadiene monomers and the catalyst, together with a solvent, in a reaction chamber, and subjecting them to reaction by suitably selecting a reaction temperature in a range of 5 to 60°C and a reaction pressure in a range of atmospheric pressure to 70 and several atm so as to obtain the above-described Mooney viscosity.

[0037] In the case of adding another rubber particularly, the polybutadiene component (b) to the polybutadiene component (a) for forming the main rubber, the added amount of the polybutadiene may be in a range of 90 mass% or less, preferably, 80 mass% or less, more preferably, 70 mass% or less, most preferably, 60 mass% or less, with the lower limit being in a range of 10 mass% or more, preferably, 20 mass% or more, more preferably, 30 mass% or more, most preferably, 40 mass% or more.

[0038] A suitable rubber composition is typically obtained by adding an unsaturated carboxylic acid and/or a metal salt thereof and an organic peroxide as essential components to the main rubber containing a specific amount of the polybutadiene component (a). A hot-molded product obtained from such a rubber composition is excellent in resilience, with a result that a golf ball including the hot-molded product becomes excellent in resilience.

[0039] Examples of the unsaturated carboxylic acids may include acrylic acid, metacrylic acid, maleic acid, fumaric acid. In particular, acrylic acid and metacrylic acid are preferably used.

[0040] Examples of the metal salts of unsaturated carboxylic acids may include zinc salts and magnesium salts of unsaturated aliphatic acids, for example, zinc metacrylate and zinc acrylate. In particular, zinc acrylate is preferably used.

[0041] The content of the unsaturated carboxylic acid and/or metal salt thereof may be set, on the basis of 100 parts by mass of the main rubber, in a range of 10 parts by mass or more, preferably, 15 parts by mass or more, more preferably, 20 parts by mass or more, with the upper limit being in a range of 60 parts by mass or less, preferably, 50 parts by mass or less, more preferably, 45 parts by mass or less, most preferably, 40 parts by mass or less. If the content is excessively small, the resilience is reduced, and if excessively large, the golf ball becomes excessively hard, which may make player's feeling of hitting of the golf ball undesirable.

[0042] As the organic peroxide, there can be used a commercial product such as "Percumyl D" (sold by NOF CORPORATION), "Perhexa 3M" (sold by NOF CORPORATION), "Luperco 231XL" (sold by Elf Atochem Japan). Two kinds or more organic peroxides may be used in combination as needed.

[0043] The content of the organic peroxide may be set, on the basis of 100 parts by mass of the main rubber containing the polybutadiene component (a) as an essential component, in a range of 0.1 part by mass or more, preferably, 0.3 part by mass or more, more preferably, 0.5 part by mass or more, most preferably, 0.7 part by mass or more, with the upper limit being in a range of 5 parts by mass or less, preferably, 4 parts by mass or less, more preferably, 3 parts by mass or less, most preferably, 2 parts by mass or less. If the content is excessively large or small, the resilience, player's feeling of hitting the golf ball, and durability may be degraded.

[0044] In addition to the above-described essential components, an inorganic filler can be added to the rubber composition of the present invention for adjusting the specific gravity, as needed. Examples of the inorganic fillers may include zinc oxide, barium sulfate, and calcium carbonate. In order to obtain a suitable weight and desirable resilience, the content of the inorganic filler may be set, on the basis of 100 parts by mass of the main rubber containing the polybutadiene component (a) as an essential component, in a range of 1 part by mass or more, preferably, 3 parts by mass or more, more preferably, 5 parts by mass or more, most preferably, 7 parts by mass or more, with the upper limit being in a range of 130 parts by mass or less, preferably, 50 parts by mass or less, more preferably, 45 parts by mass or less, most preferably, 40 parts by mass or less.

[0045] An antioxidant may be further added to the rubber composition of the present invention, as needed. As the antioxidant, there can be used a commercial product such as "NOCRAC NS-6, NS-30" (sold by Ouchi-Sinko Chemical Industrial Co., Ltd.), or "Yoshinox 425" (Yoshitomi Pharmaceutical Co., Ltd.). In order to obtain desirable resilience and durability, the content of the antioxidant may be set, on the basis of 100 parts by mass of the main rubber containing the polybutadiene component (a) as an essential component, in a range of 0 part by mass or more, preferably, 0.05 part by mass or more, more preferably, 0.1 part by mass or more, most preferably, 0.2 part by mass or more, with the upper limit being in a range of 3 parts by mass or less, preferably, 2 parts by mass or less, more preferably, 1 part by mass or less, most preferably, 0.5 part by mass or less.

[0046] The rubber composition of the present invention can further contain an organic sulfur compound. Examples of the organic sulfur compounds may include thiophenol, thionaphthol, halogenated thiophenol, or metal salts thereof, more concretely, zinc salts of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, and parachlorothiophenol; and diphenyl polysulfide, dibenzil polysulfide, dibenzoil polysulfide, dibenzothiazoil polysulfide, and dithiobenzoil polysulfide, each of which has the sulfur number of 2 to 4. In particular, a zinc salt of pentachlorothiophenol or diphenyl disulfide is preferably used. The content of the organic sulfur compound may be set, on the basis of 100 parts

by mass of the main rubber obtained by mixing the polybutadiene component (a) as an essential component with the polybutadiene component (b) at a specific mixing ratio, in a range of 0.1 part by mass or more, preferably, 0.2 part by mass or more, more preferably, 0.5 part by mass or more, with the upper limit being in a range of 5 parts by mass or less, preferably, 4 parts by mass or less, more preferably, 3 parts by mass or less, most preferably, 2 parts by mass or less.

[0047] The hot-molded product can usually be obtained by vulcanizing and heating the above-described rubber composition by a known process. For example, a vulcanizing temperature may be set in a range of 100 to 200°C, and a vulcanizing time be set in a range of 10 to 40 min.

[0048] The hardness of the hot-molded product can be suitably adjusted in accordance with the usage form (to be described later) of a golf ball, and is not particularly limited. For example, the sectional hardness of the hot-molded product may be uniform from the center to the surface of the molded-product, or a difference in sectional hardness may be present between the center and the surface of the molded-product. Typically and generally, however, the flexion or deformation of a body of the hot-molded product, measured (e.g. as in the Examples) by applying a load of 980 N (100 kg) thereto between flat plates, may be in a range of 2.0 mm or more, preferably, 2.5 mm or more, more preferably, 2.8 mm or more, most preferably, 3.2 mm or more, with the upper limit being in a range of 6.0 mm or less, preferably, 5.5 mm or less, more preferably, 5.0 mm or less, most preferably, 4.5 mm or less. If the flexural amount, that is, the deformed amount is excessively small, player's feeling of hitting the golf ball becomes worse, and particularly, the spin of the ball becomes excessively high at the time of long-shot with a driver when the ball is liable to be largely deformed, to reduce the carry of the ball, and if the deformed amount is excessively large, that is, if the golf ball becomes excessively soft, player's feeling of hitting the ball becomes dull, the carry of the ball is reduced because of insufficient resilience, and durability against cracking due to repeated hitting may become worse.

[0049] The golf ball of the present invention is characterized by including the above hot-molded product as a composing element, and the form of the ball is not particularly limited. To be more specific, the golf ball of the present invention may be any of a one-piece golf ball in which the hot-molded product is directly applied to the golf ball, a two-piece solid golf ball in which the hot-molded product is used as a solid core on the surface of which a cover is formed, a multi-piece solid golf ball having three-pieces or more in which the hot-molded product is used as a solid core on the surface of which two or more cover layers are formed, and a bobbin type golf ball in which the hot-molded product is used as a center core. In particular, from the viewpoint of making effective use of the hot-molded product to improve the moldability in extrusion of the rubber composition and give excellent resilience to the ball, the golf ball of the present invention is preferably used in the form of a two-piece solid golf ball or a multi-piece solid golf ball.

[0050] Preferably, in the case of using the hot-molded product as a solid core, the diameter of the solid core may be in a range of 30.0 mm or more, preferably, 32.0 mm or more, more preferably, 35.0 mm or more, most preferably, 37.0 mm or more, with the upper limit being in a range of 41.0 mm or less, preferably, 40.5 mm or less, more preferably, 40.0 mm or less, most preferably, 39.5 mm or less. In particular, the diameter of the solid core used for a two-piece solid golf ball may be in a range of 37.0 mm or more, preferably, 37.5 mm or more, more preferably, 38.0 mm or more, most preferably, 38.5 mm or more, with the upper limit being in a range of 41.0 mm or less, preferably, 40.5 mm or less, more preferably, 40.0 mm or less; and the diameter of the solid core used for a three-piece solid golf ball may be in a range of 30.0 mm or less, preferably, 32.0 mm or less, more preferably, 34.0 mm or more, most preferably, 35.0 mm or more, with the upper limit being in a range of 40.0 mm or less, preferably, 39.5 mm or less, more preferably, 39.0 mm or less.

[0051] The specific gravity of the solid core may be in a range of 0.9 or more, preferably, 1.0 or more, more preferably, 1.1 or more, with the upper limit being in a range of 1.4 or less, preferably, 1.3 or less, more preferably, 1.2 or less.

[0052] In the case where the golf ball of the present invention is applied to a two-piece solid golf ball or a multi-piece solid golf ball, the golf ball can be produced by putting a solid core formed of the hot-molded product, and injecting-molding or press-molding a known cover material, or a known cover material and a known intermediate layer material on the solid core.

[0053] As a main material of each of the cover material and intermediate layer material, there may be used a thermoplastic or thermosetting polyurethane based elastomer, a polyester based elastomer, an ionomer resin, a polyolefine based elastomer, or a mixture thereof. These materials may be used singly or in combination of two kinds or more. In particular, the thermoplastic polyurethane elastomer or ionomer resin is preferably used.

[0054] As the thermoplastic polyurethane based elastomer, there can be used a commercial product such as an elastomer containing aliphatic or aromatic diisocyanate, for example, "Pandex T7298, T7295, T7890, TR3080, T8295, or T8290" (sold by DIC-Bayer Polymer Co., Ltd.). As the ionomer resin, there can be used a commercial product such as "Surlyn 6320, or 8120" (sold by Du Pont DE NEMOURS & COMPANY, USA), or "Himilan 1706, 1605, 1855, 1601, or 1557" (sold by Du Pont-Mitsui Polychemicals Co., Ltd.).

[0055] Another polymer such as a thermoplastic elastomer other than that described above may be added, as an arbitrary component, to the main material of each of the cover material and intermediate layer material. Examples of such polymers may include a polyamide based elastomer, a styrene based block elastomer, a hydrogenated poly-

utadiene, and an ethylene-vinyl acetate (EVA) copolymer.

[0056] A golf ball using the present rubber composition, which is generally applied to a two-piece solid golf ball or a multi-piece solid golf ball, can be produced in accordance with a known process. While not particularly limited, the two-piece solid golf ball can be produced by putting a solid core formed of the hot-molded product in a specific injection-molding mold, and injecting the above cover material thereon by a specific known manner, and the multi-piece solid golf ball can be produced by putting a solid core formed of the hot-molded product in a specific injection-molding mold and sequentially injecting the above intermediate layer and cover material thereon by a specific manner. Alternatively, the cover material is formed on the solid core by press-molding.

[0057] The thickness of the intermediate layer used for a multi-piece solid golf ball may be in a range of 0.5 mm or more, preferably, 1.0 mm or more, with the upper limit being in a range of 3.0 mm or less, preferably, 2.5 mm or less, more preferably, 2.0 mm or less, most preferably, 1.6 mm or less.

[0058] The thickness of the cover used for a two-piece solid golf ball or multi-piece solid golf ball may be in a range of 0.7 mm or more, preferably, 1.0 mm or more, with the upper limit being in a range of 3.0 mm or less, preferably, 2.5 mm or less, more preferably, 2.0 mm or less, most preferably, 1.6 mm or less.

[0059] The golf ball of the present invention can be produced with its diameter and weight specified under a golf rule for golf games. Concretely, the diameter of the golf ball can be set in a range of 42.67 mm or more, with the upper limit being in a range of 44.0 mm or less, preferably, 43.5 mm or less, more preferably, 43.0 mm or less, and the weight of the golf ball can be set in a range of 45.93 g or less, with the lower limit being in a range of 44.5 g or more, preferably, 45.0 g or more, more preferably, 45.1 g or more, most preferably, 45.2 g or more.

EXAMPLE

[0060] The present invention will be more clearly understood by way of, while not limited thereto, the following examples and comparative examples.

Examples 1 to 7 and Comparative Examples 1 to 6

[0061] A rubber composition for a solid core was prepared by adding core materials shown in Table 2 to 100 parts by mass of each of polybutadiene components obtained by mixing polybutadienes of the following kinds (1) to (7) having physical properties shown in Table 1 at each mixing ratio shown in Table 2, and a solid core was produced from the rubber composition. In Table 2, "Percumyl D" (sold by NOF CORPORATION) was used as dicumyl peroxide, and "NOCRAK NS-6" (sold by Ouchi-Sinko Chemical Industrial Co., Ltd.) was used as an antioxidant.

Kinds of Polybutadienes

[0062]

- (1) polybutadiene: "BR01" (sold by JSR Co., Ltd.)
- (2) polybutadiene: "BR11" (sold by JSR Co., Ltd.)
- (3) polybutadiene: "UBE101" (sold by Ube Industries, Ltd.)
- (4) polybutadiene: "BR18" (sold by JSR Co., Ltd.)
- (5) polybutadiene: "HCBN-5 (trial grade)" (sold by JSR Co., Ltd.)
- (6) polybutadiene: "HCBN-2 (trial grade)" (sold by JSR Co., Ltd.)
- (7) polybutadiene: "HCBN-4 (trial grade)" (sold by JSR Co., Ltd.)

Table 1

	Kind	Catalyst	Cis-1,4-Structure (%)	Mooney Viscosity (ML)	20xML-600	η
Polybutadiene	(1)	Ni	96	44	280	150
	(2)	Ni	96	44	280	270
	(3)	Co	95	38	160	130
	(4)	Ni	96	60	600	590
	(5)	Nd	96	42	240	150
	(6)	Nd	96	40	200	280
	(7)	Nd	96	44	280	390

Table 2

	Kind	Examples							Comparative Examples					
		1	2	3	4	5	6	7	1	2	3	4	5	6
Polybutadiene Composition (mass %)	(1)					50				40		50	50	50
	(2)	20	50	40				50				50		
	(3)						50						50	50
	(4)				50						50			
	(5)									60	50			
	(6)	80	50		50	50	50	50	100					
	(7)			60										
Core Composition (parts by mass)	Polybutadiene	100	100	100	100	100	100	100	100	100	100	100	100	100
	Dicumyl Peroxide	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
	Zinc Oxide	22	22	22	22	22	22	34.5	22	22	22	22	22	34.5
	Anti-oxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	Zinc Acrylate	24	24	24	24	24	24	24	24	24	24	24	24	24

[0063] The rubber composition for a solid core was then suitably kneaded by a kneader or a roll, and the workability at the time of extruding a specific amount of the rubber composition was evaluated under the following criteria. The results are shown in Table 3.

Evaluation of Workability in Extrusion

[0064] The surface and shape of a slug obtained by extruding the rubber composition were evaluated under the following criteria:

- Grade 5: the workability in extrusion is very good and the slug surface is good.
 Grade 4: the workability in extrusion is good and the slug surface is slightly rough.

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Grade 3: the rubber composition is extrudable but scuffing occurs on the slug surface.

Grade 2: the rubber composition is extrudable but scuffing on the slug surface is very conspicuous.

Grade 1: A failure in shape of the slug occurs, and it is difficult to extrude a specific amount of the rubber composition.

[0065] In each of Examples 1 to 6 and Comparative Example 1 to 5, a solid core having a diameter of about 38.9 mm and a weight of about 36.0 g was produced by using the above rubber composition for a solid core, and in each of Example 7 and Comparative Example 6, a solid core having a diameter of 35.3 mm and a weight of 31.0 g was produced by using the above rubber composition.

[0066] The press-molding of the rubber composition was performed at 150°C for 20 min.

[0067] A deformed amount of the solid core thus obtained, measured by applying a load of 980 N (100 kg) thereto, was examined, and further the resilience of the solid core was examined as follows. The results are shown in Table 3.

Flexural Amount (Load: 980 N)

[0068] A deformed amount (mm) of the solid core, measured by applying a load of 980 N (100 kg), was measured.

Resilience

[0069] The initial velocity of a golf ball obtained by using the above solid core was measured by an initial velocity meter of the same type as that used in a certified institution USGA. For each of Examples 1 to 6 and Comparative Examples 1 to 5, the resilience was expressed by a differential initial velocity based on an initial velocity in Comparative Example 4. For Example 7, the resilience was expressed by a differential initial velocity based on an initial velocity of Comparative Example 6.

[0070] In each of Examples 1 to 6 and Comparative Examples 1 to 5, the solid core was put in a specific mold, and a cover material (Himilan 1601/Himilan 1557 = 50/50) was injection-molded thereon, to produce a two-piece solid golf ball having a diameter of 42.7 mm and a weight of 45.3 g. In each of Example 7 and Comparative Example 6, the solid core was put in the same specific mold as described above and an intermediate layer material (Himilan 1706/Himilan 1605 = 50/50) was injection-molded thereon, to produce an intermediate layer covered core having a diameter of about 38.7 mm, and then the intermediate layer covered core was shifted in a specific mold and a cover material (Himilan 1650/Surlyn 8120 = 50/50) was injection-molded thereon, to produce a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g.

[0071] The carrying performance of each of the golf balls thus obtained was examined. The results are shown in Table 3.

Physical Properties of Golf Ball

[0072] Each golf ball was hit at a head speed of 45 m/s by a hitting machine on which a driver (W#1) was previously mounted, and the carry and total distance of the hit ball were measured.

[0073] As shown in Table 3, it was found that the golf ball of the present invention can exhibit excellent resilience.

Table 3

		Examples							Comparative Examples					
		1	2	3	4	5	6	7	1	2	3	4	5	6
Solid Core	Flexural Amount (mm) (load: 980N)	3.4	3.5	3.5	3.6	3.5	3.5	3.1	3.3	3.4	3.6	3.7	3.7	3.3
	Resilience (m/s)	+0.6	+0.5	+0.4	+0.6	+0.4	+0.4	+0.5	+0.6	+0.3	+0.4	0	0	0
	Workability in Extrusion	3	4	4	2	3	3	4	1	2	1	5	4	4
Physical Properties of Golf Ball (HS45)	Carry (m)	213.3	213.1	213.0	213.2	212.7	212.5	213.5	213.1	212.3	212.5	209.5	209.2	209.5
	Total (m)	226.9	226.8	226.8	226.9	226.4	226.2	227.3	226.7	225.7	226.0	223.3	223.0	223.6

Claims

1. A golf ball comprising a body hot-molded from a rubber composition comprising a base rubber; unsaturated carboxylic acid and/or metal salt thereof; and organic peroxide; wherein said base rubber contains from 10 to 90 mass% of polybutadiene (a) which has 60% or more of cis-1,4- bond; and for which a Mooney viscosity ML and a solution viscosity value η satisfy the relationship $\eta \geq 20 \times ML - 600$; ML being the Mooney viscosity ($ML_{1+4}(100^\circ C)$) and η mPa-s being the viscosity at $25^\circ C$ of a 5 mass% toluene solution of the polybutadiene.
2. A golf ball according to claim 1 wherein said polybutadiene (a) is rare earth-catalysed polybutadiene.
3. A golf ball according to claim 2, wherein said polybutadiene (a) is one synthesized using a rare earth element based catalyst, and then reacted with a terminal denaturant.
4. A golf ball according to any one of claims 1 to 3 wherein said base rubber contains, in addition to said polybutadiene (a), 90 to 10 mass% of other polybutadiene (b) having a Mooney viscosity of 55 to less.
5. A golf ball according to any one of the preceding claims which is a two-piece, three-piece or multi-piece ball in which said body is a core component.
6. A method of making a golf ball according to any one of claims 1 to 5, including the step of moulding the rubber composition to form said body.
7. A method according to claim 6 including the step of blending the rubber composition from the base rubber.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 30 7879

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	US 4 683 257 A (KAKIUCHI SHINICHI ET AL) 28 July 1987 (1987-07-28) * abstract; claims 1-5 * * column 1, line 7-36 * * column 2, line 24-28 * * column 3, line 41-65 * * column 5, line 54-65 * * column 6, line 3-16 * ---	1-7	C08L9/00 A63B37/00
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 05, 14 September 2000 (2000-09-14) & JP 2000 042141 A (SUMITOMO RUBBER IND LTD), 15 February 2000 (2000-02-15) * abstract; claims 1-4 * ---	1-3,5-7	
X	EP 0 605 162 A (SUMITOMO RUBBER IND) 6 July 1994 (1994-07-06) * abstract; claims 1-9 * * page 3, line 19-21,34-50 * * page 4, line 13-16 * * page 10, line 2-10 * ---	1-3,5-7 4	
A			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
P,X	WO 01 52946 A (SPALDING SPORTS WORLDWIDE INC) 26 July 2001 (2001-07-26) * abstract; claims 1-16 * * page 8, line 1-15 * * page 9, line 5-16 * * page 11, line 9-20 * * page 12, line 11-14 * * page 13, line 11 * ---	1-7	C08L A63B
A	EP 1 031 583 A (KOREA KUMHO PETROCHEM CO LTD) 30 August 2000 (2000-08-30) * abstract; claims 1-7 * * page 6; table 4 * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 February 2002	Examiner Bergmans, K
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background C: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application I: document cited for other reasons &: member of the same patent family, corresponding document			

EPC FORM 1503 (3.12.02) (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 7879

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-02-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4683257	A	28-07-1987	JP	1981581 C	25-10-1995
			JP	6080123 B	12-10-1994
			JP	62089750 A	24-04-1987

JP 2000042141	A	15-02-2000	US	6315679 B1	13-11-2001

EP 0605162	A	06-07-1994	JP	6190083 A	12-07-1994
			AU	664933 B2	07-12-1995
			AU	5259293 A	07-07-1994
			CA	2111806 A1	26-06-1994
			DE	69312245 D1	21-08-1997
			DE	69312245 T2	04-12-1997
			EP	0605162 A1	06-07-1994
			US	5585440 A	17-12-1996

WO 0152946	A	26-07-2001	AU	5790701 A	31-07-2001
			WO	0152946 A1	26-07-2001

EP 1031583	A	30-08-2000	EP	1031583 A1	30-08-2000
			US	6136931 A	24-10-2000

EPC FORM P0408

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82